

- Final Report -

# **Macroscopic Synthesis of Metal Cluster Materials AASERT Program**

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## 13. ABSTRACT (Maximum 200 Words)

Various prospects have been investigated for potential isolation as cluster-based materials. Gas phase molecular beam experiments have investigated metal carbide and metal oxide clusters (TiC, TiO<sub>2</sub>, VC, MgO, Al<sub>2</sub>O<sub>3</sub>, etc.) as well as transition metal complexes with C<sub>60</sub> and with polycyclic aromatic hydrocarbons (PAH's). New measurements including infrared resonance enhanced ionization spectroscopy with a free electron laser have been applied to these systems. A new laser vaporization flow tube reactor has been constructed which allows high densities of clusters to be produced and stabilized via ligand coating techniques. Soluble metal-containing compounds have been produced and analyzed with laser desorption mass spectrometry. However, further work will be required to achieve isolation of pure cluster materials.

## 14. SUBJECT TERMS

metal complexes, metal clusters, nanoparticle synthesis

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## OBJECTIVES

This project investigates the structure and bonding in stable metal containing clusters which may be used as precursors for cluster materials of various kinds. Clusters are evaluated for their stability by gas phase molecular beam experiments. Those with promising characteristics are targeted for macroscopic synthesis in a new high throughput Laser Vaporization Flowtube Reactor (LAFR). Target species for investigation include metal compound clusters (carbides, oxides, etc.) and novel organometallic cluster complexes (metal-C<sub>60</sub>, metal-polycyclic aromatic hydrocarbons, etc.). The overall goal of this project is to identify, synthesize, isolate and characterize new materials based on clusters which cannot be produced by conventional synthetic methods.

## STATUS OF EFFORT

Survey experiments using a laser vaporization cluster source, a pulsed molecular beam apparatus and laser ionization time-of-flight mass spectrometry measurements have been in progress for some time. These experiments have identified several classes of clusters promising for isolation including metal carbides of the early transition metals, exohedral transition metal-C<sub>60</sub> complexes and transition metal-polyaromatic (PAH) complexes. Mass spectroscopy and mass-selected photodissociation measurements have been applied to characterize cluster stability in these systems. These experiments in the gas phase are continuing to investigate new cluster systems. On the synthetic side, we have completed the construction of a new instrument for the production and isolation of

macroscopic cluster materials, which we designate as the Laser Vaporization Flowtube Reactor (LAFR). Experiments on this device have led to several design modifications and eventually to the production of our first isolated samples. The samples isolated already suggest the production of previously unknown metal cluster materials. However, optimization of the instrument and the methodology need to be continued, especially with regard to the handling of air sensitive samples.

## ACCOMPLISHMENTS/NEW FINDINGS

### *Metal Carbide Clusters*

Previous studies in our group and others have demonstrated the surprising stability of metal carbide clusters which have the special stoichiometries of  $M_8C_{12}$  and  $M_{14}C_{13}$  (the so-called "met-cars" and "nanocrystal" metal carbides). The tendency to form these species is especially strong for the early transition metals. Experiment and theory suggest that these metal compound clusters have special stability, but none of these systems have been isolated. We therefore embarked on an ambitious effort to scale up cluster production and to make macroscopic amounts of these kinds of clusters. The apparatus constructed for these studies appears in Figure 1. It is a flow-tube reactor with a high-repetition rate (100 Hz) excimer laser for high-throughput laser ablation in the source. This essential laser was provided by the University of Georgia Research Foundation (UGARF). To facilitate the production of macroscopic amounts of clusters, this instrument uses a high repetition rate pulsed source together with a continuous spray of inert gas for collisional stabilization of clusters as they grow. An additional strategy is the use of a ligand spray

provided by a liquid→gas nebulizer to coat or sequester highly reactive clusters. This approach is needed for clusters such as the met-cars, where there is intrinsic bonding stability but high reactivity due to exposed transition metals. Ligand coatings are expected to stabilize the clusters and to provide solubility to enhance the possibilities for isolation and purification. The instrument has an oven source in addition to the laser vaporization source for the simultaneous addition of involatile ligand species (e.g. fullerenes, polycyclic aromatic hydrocarbons, PAH's) for reaction with vaporized metal. Initial experiments on this machine have been conducted, and several preliminary results have been obtained. A postdoc working on this project has been funded by UGARF.

Figures 2 and 3 show the results of experiment, when titanium clusters are produced and exposed to different ligand species. These experiments were done as a precursor to the studies on titanium-carbide clusters. The data in Figure 2 was generated via laser vaporization of a titanium sample with a ligand spray of ethylenediamine (en) in THF. A blue oil was isolated in the liquid nitrogen-cooled trap, which was insoluble in several organic solvents tested. However, when a small amount of the oil was interrogated with laser vaporization mass spectrometry, a surprisingly simple mass spectrum was observed, as shown in Figure 2. In the low mass range, there are titanium and titanium oxide peaks as well as alkali metal impurities. However, in the higher mass range there is a series of three peaks whose masses are consistent with  $Ti_x(en)_y^+$  ions. Ethylenediamine is a bidentate ligand, and therefore the stoichiometries observed can be rationalized with simple structures. The  $Ti(en)_3$  mass could clearly be explained by sixfold coordination with an octahedral configuration around the metal. Likewise, the  $Ti_2(en)_5$  and  $Ti_3(en)_7$  species can also be explained with sixfold coordination about the metal with the titanium atoms

connected by single bonds (i.e., Ti-Ti and Ti-Ti-Ti core units). Figure 3 shows a similar result obtained when titanium is vaporized and there is only the THF solution present in the ligand spray. Again, a simple mass spectrum is obtained which has multiples of the mass 209. This mass can be assigned to  $\text{TiO(THF)}_2$ , as indicated in the insert. A plausible assignment for this mass is a polymer which repeats this building block, as indicated in the figure. It is not known whether the oxygen here comes from the THF or from an air leak.

Unfortunately, these suggested structures for titanium clusters with ethylenediamine and THF may not be the only possibilities for these masses. Additionally, much further work is required to reproduce these results, to optimize the conditions for these species and to characterize them structurally. These materials need to be isolated and characterized via standard chemical methods. Initial indications are, however, that these materials are air sensitive. This severely limits our ability to isolate and purify them. However, these preliminary results show that novel species can be produced and isolated with the LAFR instrument. No complexes of titanium and ethylenediamine or THF has ever been isolated, and such species are expected to have unusual properties. Experiments in the future may need to employ a dry box for sample handling, and efforts to secure such a system are in progress. Until such capabilities are in place, we do not anticipate success with the ultimate goal of isolating metal carbide clusters of titanium or vanadium.

In other gas phase work on metal carbides, this PI went to Holland in May-June 1999 as a Visiting Research Professor at the University of Nijmegen. In a collaboration with Professor Gerard Meijer and his group, we built a new molecular beam/metal cluster experiment at the "FELIX" free electron laser facility at the F.O.M. Institute for Plasma Physics in Utrecht. The FELIX laser is the only free electron laser worldwide which is

conveniently tunable. Free electron lasers provide infrared light in the  $100\text{--}2000\text{ cm}^{-1}$  region where the low frequency vibrations of metal clusters are expected. Initial experiments produced spectacular results. Using the technique of infrared resonance-enhance multi-photon ionization (IR-REMPI), we were able to measure IR action spectra for the met-cars species  $\text{Ti}_8\text{C}_{12}$  and  $\text{V}_8\text{C}_{12}$  and their  $^{13}\text{C}$  substituted isotopomers. IR-REMPI is possible in these clusters because they are so strongly bound. Multiple photon absorption therefore leads eventually to ionization (known as "thermionic emission") rather than fragmentation. These represent the first spectroscopic data for the met-cars species other than low-resolution photoelectron spectra. Additionally, these experiments represent the first infrared spectra ever recorded for gas phase metal clusters. Other spectra were also measured for the  $\text{Ti}_{14}\text{C}_{13}$  and  $\text{V}_{14}\text{C}_{13}$  "nanocrystal" clusters and for a collection of many larger but less prominent nanocrystal masses, including clusters of over 100 atoms in size! These spectra provide the first experimental insight into the structures of these clusters. The IR spectra of the met-cars species have a giant resonance near  $1400\text{ cm}^{-1}$ , which is assigned to a C-C stretching mode. Theory has predicted the presence of  $\text{C}_2$  moieties along the edges of these clusters, and this result confirms that  $\text{C}_2$  groups are present. In the nanocrystal clusters, no high frequency vibrations are detected. Instead, resonances at  $500$  and  $650\text{ cm}^{-1}$  are measured. Significantly, these occur at exactly the positions of the known surface phonon bands in bulk TiC and VC (measured previously with EELS). This observation confirms that these clusters have the crystal-fragment structures suggested previously.

A surprising outgrowth of this work came when the spectrum of larger TiC nanocrystal clusters were examined with IR-REMPI. It was discovered that the spectrum of

the 14/13 species changed only gradually in larger clusters. The  $500\text{ cm}^{-1}$  band became stronger and more intense, while the  $650\text{ cm}^{-1}$  feature became a weak shoulder. However, the  $500\text{ cm}^{-1}$  feature comes at essentially the same frequency for all clusters up to 125 atoms in size (i.e., the  $5\times 5\times 5$  species). Moreover, via an accidental encounter with astronomer Alexander Tielens (University of Groningen, The Netherlands), this spectrum was eventually assigned as the carrier of the previously unidentified "21 micron line" seen in the IR spectra of so-called post-AGB stars which are rich in carbon. This work therefore shows convincingly that TiC nanocrystals are formed at an early stage of dust formation in these kinds of stars.

~~=====~~ This new IR-REMPI work has significant implications for the possible isolation of metcars and nanocrystal species. Prior to this work, there was considerable uncertainty about the relative stability of neutral versus cationic metcars clusters, and the nanocrystal species were assumed to be stable only as neutrals. However, these experiments demonstrate unequivocally that both kinds of clusters are stable as neutrals, which is advantageous for their isolation.

This PI made another visit to The Netherlands in the summer of 2000 to follow up on the initial success of the previous summer. In this new work, various metal oxide clusters were studied with the IR-REMPI technique. We were pleased to find that the technique is also successful for these studies. New vibrational spectra were obtained for  $(\text{MgO})_n$ ,  $(\text{Al}_2\text{O}_3)_n$  and  $(\text{TiO}_2)_n$  clusters out to over 200 atoms in size. These data provide spectra which in some cases can be compared to surface phonon spectra of the corresponding bulk metal oxide surfaces measured with electron energy loss spectroscopy (EELS). This data is under analysis at present.

### *Metal-Fullerene Clusters and Metal-Polyaromatic Hydrocarbon Clusters*

Another exciting project made it possible to produce novel organometallic clusters, which may also be attractive candidates for isolation as macroscopic materials. Laser vaporization of composite samples composed of a metal rod coated with a thin film of involatile organic species has made it possible to produce a variety of metal/organic mixed clusters. Some of the fascinating species produced include metal- $C_{60}$  complexes (exohedral) and metal-polyaromatic hydrocarbon (PAH) species. Metal- $C_{60}$  species have been studied previously by T.P. Martin and coworkers, and Kaya and coworkers, but our lab has provided the first photodissociation studies to probe the structure and bonding in these species. We have focused on metal-PAH complexes with the symmetric PAH molecule coronene ( $C_{24}H_{12}$ ; seven rings with  $D_{6h}$  symmetry) and also with pyrene. Two general kinds of photodissociation behavior have been observed. In some  $M_x(\text{PAH})_y$  complexes, photodissociation leads to elimination of intact metal clusters,  $M_x^+$ , while in others only atomic metal species are eliminated. Silver complexes with coronene exhibit pure molecular metal elimination, while iron-coronene complexes exhibit pure atomic metal elimination. However, most other transition metals (cobalt, nickel, iron)  $[M_x-C_{60}]^+$  clusters eliminate a distribution of fragment metal species including atoms, diatomics, ..., all the way up to  $M_x^+$ . Niobium and calcium complexes are different again in that metal carbide masses are eliminated, presumably because the metal inserts into the aromatic ring system. In several of these systems there is evidence for sandwich and multi-decker sandwich masses. A particularly interesting species is  $Cr_3(\text{coronene})_2$  which is believed to be a sandwich with three included metal atoms. This species exhibits surprising stability and it may be possible to isolate it via future LAFR experiments.

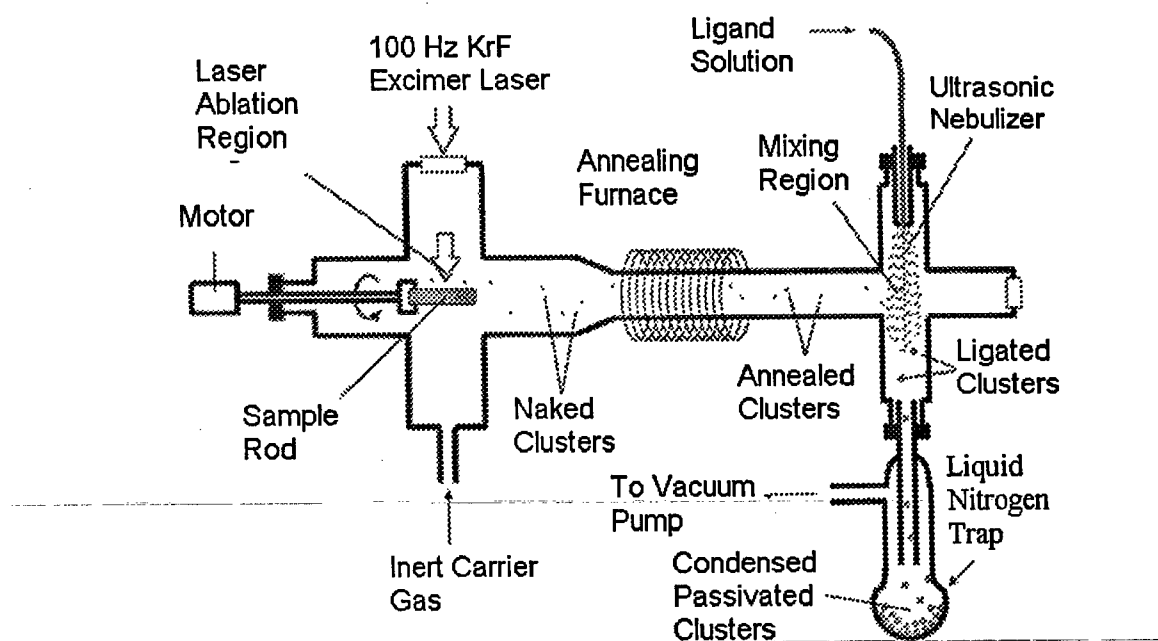


Figure 1. The laser vaporization flow tube reactor used for synthesis of macroscopic cluster materials.

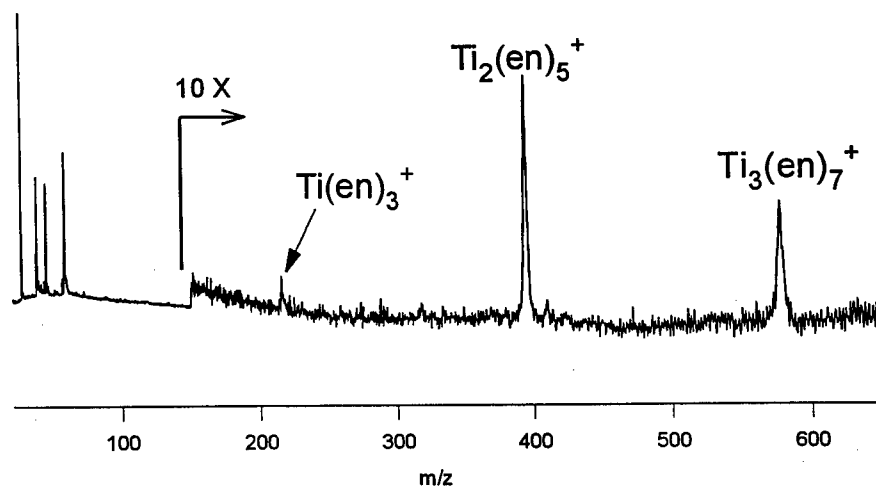


Figure 2. The mass spectrum recorded for titanium clusters produced and trapped with ethylene diamine as a ligand.

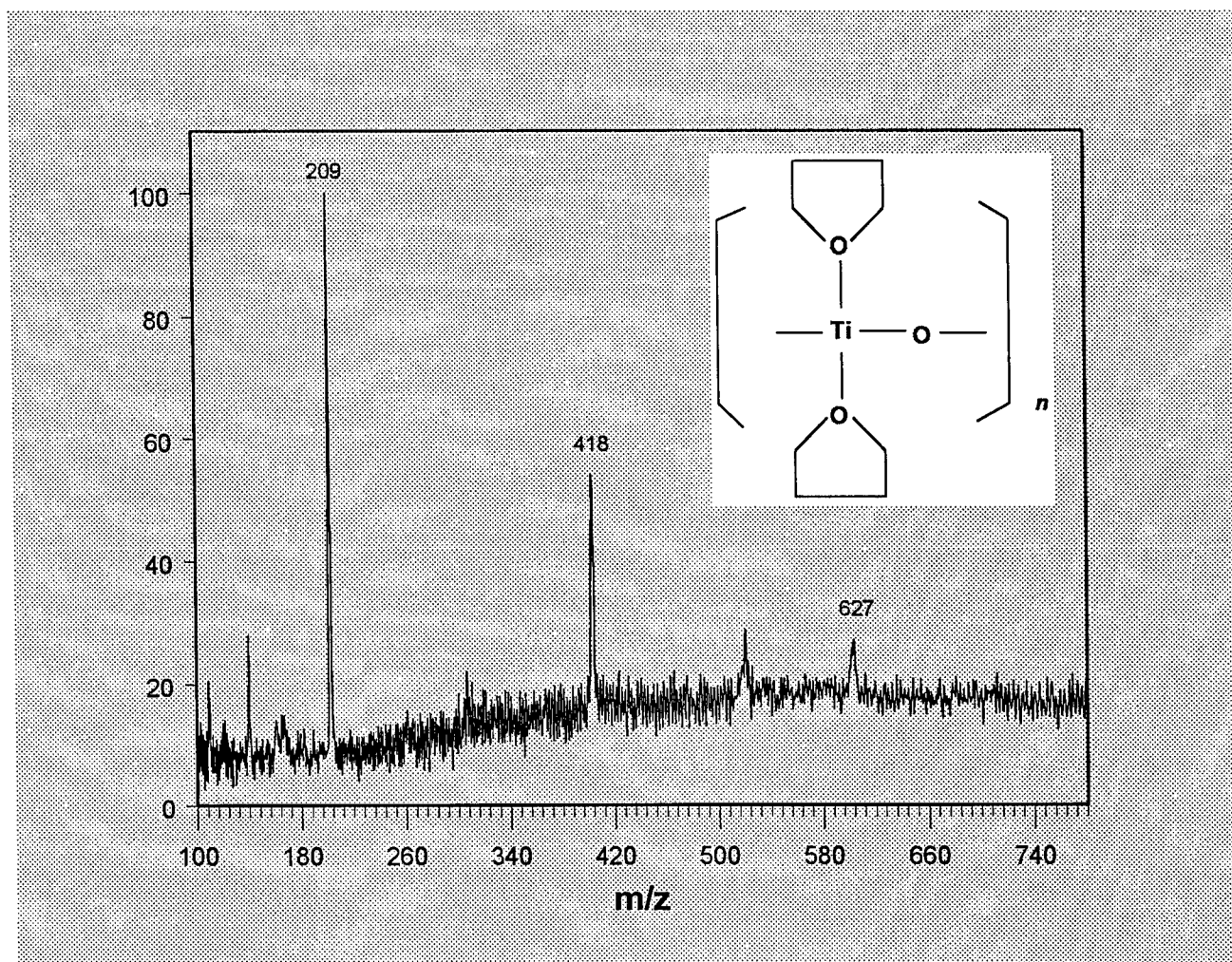


Figure 3. The mass spectrum recorded for titanium clusters produced and trapped with THF as a ligand.

## PERSONNEL SUPPORTED BY AND/OR ASSOCIATED WITH PROJECT

### Faculty:

Professor Michael A. Duncan

### Graduate Students:

Student	Degree Program	Social Security Number
Greg Grieves	Ph.D.	[REDACTED]
Nichole McKee	M.S.	[REDACTED]

### Undergraduate Student:

Matt Nee (presently a graduate student at UC-Berkeley).

### Postdoctoral Fellows:

Dr. James Fye (Ph.D. 1998, Northwestern University)

Dr. Quan Li (Ph.D. 1998, University of Beijing, PR China)

## PUBLICATIONS IN THIS FUNDING PERIOD

1. J.W. Buchanan, J.E. Reddic, G.A. Grieves and M.A. Duncan, "Metal and Multi-Metal Complexes with Polyaromatic Hydrocarbons: Formation and Photodissociation of  $\text{Fe}_x\text{-(Coronene)}_y$  Cations," *J. Phys. Chem. A* **102**, 6390 (1998).
2. J.W. Buchanan, G.A. Grieves, J.E. Reddic and M.A. Duncan, "Novel Mixed-Ligand Sandwich Complexes: Competitive Binding of Iron with Benzene, Coronene and  $\text{C}_{60}$ ," *Intl. J. Mass Spectrom.* **182**, 323 (1999).
3. D. van Heijnsbergen, G. von Helden, M.A. Duncan, A.J.A. van Roij and G. Meijer, "Vibrational Spectroscopy of Gas Phase Metal Carbide Clusters and Nanocrystals," *Phys. Rev. Lett.* **83**, 4983 (1999).
4. G. von Helden, A.G.G.M. Tielens, D. van Heijnsbergen, M.A. Duncan, S. Hony, L.B.F.M. Waters and G. Meijer, "Titanium Carbide Nanocrystals in Circumstellar Environments," *Science* **288**, 313 (2000).
5. G.A. Grieves, J.W. Buchanan, J.E. Reddic and M.A. Duncan, "Photodissociation of exohedral transition metal- $\text{C}_{60}$  complexes," *Intl. J. Mass Spectrom.*, in press.
6. G. von Helden, A. Kirilyuk, D. van Heijnsbergen, B. Sartakov, M.A. Duncan and G. Meijer, "Infrared Spectroscopy of Gas Phase Zirconium-Oxide Clusters," *Chem. Phys.*, in press.
7. N.R. Foster, G.A. Grieves, J.W. Buchanan, N.D. Flynn and M.A. Duncan, "Growth and Photodissociation  $\text{Cr}_x\text{-(Coronene)}_y$  Complexes," *J. Phys. Chem. A* **104**, 11055 (2000).
8. G. von Helden, D. van Heijnsbergen, M.A. Duncan, A.J.A. van Roij and G. Meijer, "IR-REMPE of Vanadium Carbide Nanocrystals: Ideal versus Truncated Lattices," *Chem. Phys. Lett.*, in press.

## INTERACTIONS/TRANSITIONS

### a) PRESENTATIONS

#### Invited Lectures Presented on this Research

1. "Spectroscopy and Dynamics in Novel Metal Ion Complexes," University of Tokyo, Tokyo, Japan, October 1998.

2. "Spectroscopy and Dynamics in Novel Metal Ion Complexes," Keio University, Hiyoshi, Yokohama, Japan, October 1998.
3. "Spectroscopy and Dynamics in Novel Metal Ion Complexes," Institute for Molecular Science, Okazaki, Japan, October 1998.
4. "Spectroscopy and Dynamics in Novel Metal Ion Complexes," Tohoku University, Sendai, Japan, October 1998.
5. "Spectroscopy and Dynamics In Novel Metal Containing Clusters," *Chemistry Department Colloquium*, University of Kentucky, December 1998.
6. "Photodissociation Spectroscopy of Novel Metal Ion Complexes," *Centennial National Meeting of the American Physical Society*, Atlanta, GA, March 1999.
7. "Photodissociation Spectroscopy and Dynamics in Novel Metal Containing Cluster Complexes," Department of Atomic, Molecular and Laser Physics, University of Nijmegen, The Netherlands, May 1999.
8. "Photodissociation Spectroscopy of Novel Metal Ion Complexes," *XVIII International Symposium on Molecular Beams*, Ameland, The Netherlands, June 1999.
9. "IR-REMPI Spectroscopy of Gas Phase Metal Carbide Clusters and Nanocrystals," Symposium on *Metal Clusters: From Molecules to Nanocrystals*, Southeast Regional Meeting of the American Chemical Society, Knoxville, TN, October 1999.
10. "IR-REMPI Spectroscopy of Gas Phase Metal Carbide Clusters and Nanocrystals," *International Symposium on Cluster and Nanoparticle Interfaces*, Richmond, VA, October 1999.
11. "Photodissociation and Photoionization Spectroscopy of Gas Phase Metal Clusters," *Physical Chemistry Seminar*, University of Tennessee, Knoxville, November 1999.
12. "Synthesis and Characterization of Gas Phase Metal Clusters," *Chemistry/Physics Colloquium*, Berea College, Kentucky, November 1999.
13. "Stable Metal Carbide Nanoclusters: Photochemistry, Spectroscopy and Astrochemistry," Departmental Colloquium, West Georgia College, Carrollton, GA, February 2000.
14. "Photodissociation Spectroscopy of Novel Metal Ion Complexes," Universite Paris-Sud, Orsay, France, April 2000.
15. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," *Gordon Conference on Molecular and Ionic Clusters*, Toulouse, France, April 2000.

16. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," *Gordon Conference on Multiphoton Processes*, New Hampshire, June 2000.
17. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," School of Physics, Georgia Institute of Technology, Atlanta, August 2000.
18. "Infrared Spectroscopy of Gas Phase Metal Clusters," *Physical Chemistry Seminar*, University of Utah, September 2000.
19. "Infrared Spectroscopy of Gas Phase Metal Clusters," Pacific Northwest National Lab, Environmental Molecular Sciences Center, September 2000.
20. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," *Resonance Ionization Spectroscopy-2000*, Knoxville, TN, October 2000.
21. "IR-REMPI with a Tunable Free-Electron Laser: Vibrational Spectroscopy of Gas Phase Metal-Carbide Clusters," *International Symposium on Small Particles and Inorganic Clusters (ISSPIC-10)*, Atlanta, GA, October 2000.

#### Poster and Contributed Presentations of this Research

1. J.E. Reddic, J.C. Robinson, S.H. Pullins, G.A. Grieves and M.A. Duncan, "Production and Photodissociation of Exohedral Metal-C<sub>60</sub> Complexes in the Gas Phase," *Gordon Research Conference on Molecular and Ionic Clusters*, Ventura, CA, January 1998.
2. D. van Heijnsbergen, G. von Helden, M.A. Duncan and G. Meijer, "Infrared Resonance-Enhanced Multiphoton Ionization Spectroscopy of C<sub>60</sub> and Metal Carbide Clusters," *XVIII International Symposium on Molecular Beams*, Ameland Island, The Netherlands, June 1999.
3. D. van Heijnsbergen, G. von Helden, M.A. Duncan and G. Meijer, "Infrared Resonance-Enhanced Multiphoton Ionization Spectroscopy of Ti<sub>8</sub>C<sub>12</sub>, Ti<sub>8</sub>C<sub>11</sub> and Ti<sub>14</sub>C<sub>13</sub>: Vibrational Spectroscopy of Size-Selected Metal Carbide Clusters," *Gordon Conference on Photoions, Photoionization and Photodetachment*, Plymouth State College, New Hampshire, July 1999.
4. J.W. Buchanan, N.D. Flynn, G.A. Grieves, M. Nee and M.A. Duncan, "Photodissociation of Chromium-Coronene Cluster Cations," *Undergrad Research Symposium*, Southeast Regional Meeting of the American Chemical Society, Knoxville, TN, October 1999.
5. G.A. Grieves, J.W. Buchanan, N.D. Flynn, N. McKee and M.A. Duncan, "Production

and Photodissociation of Exohedral Metal-C<sub>60</sub> Complexes in the Gas Phase," *Symposium on Nanostructured Materials*, Georgia Institute of Technology, Atlanta, November 1999.

6. J.W. Buchanan, N. McKee, G.A. Grieves, M. Nee and M.A. Duncan, "Photodissociation of Chromium-Coronene Cluster Cations," *Symposium on Nanostructured Materials*, Georgia Institute of Technology, Atlanta, November 1999.
7. D. van Heijnsbergen, G. von Helden, M.A. Duncan and G. Meijer, "Infrared Resonance-Enhanced Multiphoton Ionization Spectroscopy of Ti<sub>8</sub>C<sub>12</sub>, Ti<sub>8</sub>C<sub>11</sub> and Ti<sub>14</sub>C<sub>13</sub>: Vibrational Spectroscopy of Size-Selected Metal Carbide Clusters," *Gordon Conference on Molecular and Ionic Clusters (MIC2000)*, Toulouse, France, April 2000.

#### **b) CONSULTATIVE AND ADVISORY FUNCTIONS**

None

#### **c) TRANSITIONS**

None

#### **NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES**

None

#### **HONORS/AWARDS – Michael A. Duncan, PI**

Yamada Foundation Visiting Professor, Keio University, Hiyoshi, Yokohama, Japan, October 1998

Visiting Professor, University of Nijmegen, The Netherlands, May-June 1999; May 2000

Appointment as Distinguished Research Professor, University of Georgia, July 2000